

## REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-08-0323

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other notice that may appear hereon, it is not intended to subject anyone to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 16-05-2008		2. REPORT TYPE Final		3. DATES COVERED (From - To) Sept 2006 - Dec 2007	
4. TITLE AND SUBTITLE Structures with Reconfigurable Circulatory Systems				5a. CONTRACT NUMBER FA9550-06-1-0552	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Clark, William W. Beckman, Eric J. Cho, Sung K. Weiland, Lisa M. Bielawski, Christopher W.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pittsburgh, 350 Thackeray Hall, Pittsburgh, PA 15260 The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 815 N Randolph St Arlington VA 22203 Dr Byung Lee/NA				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/NA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT No limitations. Distribution A: Approved for Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT In order to provide structures with new and better characteristics, researchers often look to biological systems for inspiration. One trait that many biological system have that conventional structures do not is a circulatory system, which can be used for many purposes, one of which is the transport of structural material. This project explored the possibility of enabling structures with reconfigurable transport networks by creating materials that can change from solid (load bearing state) to liquid (transport state) upon stimulus from a controlled trigger. In addition, the benefits of transporting structural material were explored analytically, for the purpose of changing the structure's static, dynamic, and shape characteristics. Results from this study indicate that it is feasible to create such state-changing materials with photonic and electrical triggers. In addition, a great deal of structural control can be achieved with such materials and transport mechanisms.					
15. SUBJECT TERMS State-changing materials, structural control, morphing, reconfigurable transport					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 27	19a. NAME OF RESPONSIBLE PERSON William W. Clark
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 412-624-9794

# **Structures with Reconfigurable Circulatory Systems**

Final Report submitted to the Air Force Office of Scientific Research

by

William W. Clark, Eric J. Beckman, Sung K. Cho, Lisa M. Weiland  
University of Pittsburgh

Christopher W. Bielawski  
University of Texas

## **A. Executive Summary**

This project focused on initial studies related to developing a novel system in which a normally stiff, load bearing structural material may be locally transformed into a liquid state, and then moved through the structure by way of distributed fluidic mechanisms. The rationale for such a system is that it will have numerous uses for structural tailoring, including healing of damage and cracks, tuning of static and dynamic structural properties, regrowth of missing or damaged parts, and even permanent shape change through mass flow. In addition, one could use the network of fluidic mechanisms proposed here as an actuation system for structural shape change.

The long-term vision is to realize this concept by developing a structure that contains an array of trigger mechanisms that can transform the solid structural material to liquid. Interspersed in this array will be another array of pumping mechanisms that can transport the liquid phase of the material. The actual flow paths will be dictated by a control system that chooses a path of structural regions that are transformed to liquid, and then actuates pumps along that path.

Key features of this concept are 1) rather than relying on a fixed flow network for the circulatory system, this approach allows the network to be arbitrarily determined, which provides an extraordinary amount of freedom in the utility of the system, 2) the concept does not rely on a reservoir of liquid that is to be moved throughout the structure, but rather enables the movement of the structural material itself. With the exception of reorganizing pumps and triggers, this concept forms the basis for structures that flow as a means of mobility or formation of arbitrary new shapes.

This report describes the work done during a nine-month project that addressed the key technical challenge to this concept, which is the development of materials that exhibit solid-to-liquid change under command of a controllable trigger. Secondary focuses of this project were different means by which the material may be moved within the structure, and an analysis of the structural changes that can be realized by such a method.

Specifically, the main objectives of the project were:

- 1) develop and demonstrate novel materials that can exhibit reversible solid-to-liquid state transition upon the command of photo and electrical triggers

**20080624 223**



- 2) to analyze, through a coupled fluidics and mechanics model, structural changes that may be realized by a reconfigurable circulatory system

## B. Description of Research

### B.1 Overview of the Reconfigurable Circulatory System Concept

#### *Concept for Incorporating a Circulatory Network*

Our concept involves a network of solid-to-liquid trigger and pumping mechanisms distributed throughout a homogeneous volume of material. One potential schematic of the proposed material system is shown in Fig. 1. By addressing a specific path of the trigger mechanisms (e.g. from A to B in Fig. 1b), the volume of material in the vicinity of that path will be transformed from solid to liquid, forming a flow channel. One or more of the pumps along that path can then be used to move the liquid that fills the channel. The material can be pumped to and from arbitrary locations in the structure for the purposes of healing defects, growing new or damaged (missing) areas, changing structural dynamic properties, or permanently changing the shape of the structure.

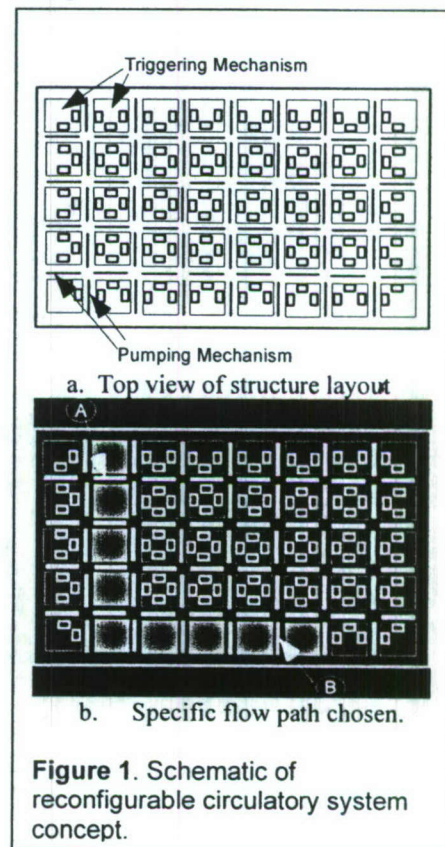
Key technical challenges that must be met to fully accomplish this concept are:

- Development of materials that exhibit solid-to-liquid change under command of a controllable trigger
- Development and integration of simplified pumping mechanisms that can be distributed within a structure
- Integration of material, pumping and trigger mechanisms to enable desirable structural tailoring
- Development of self-redistributing triggers and pumps

Key features of the concept are:

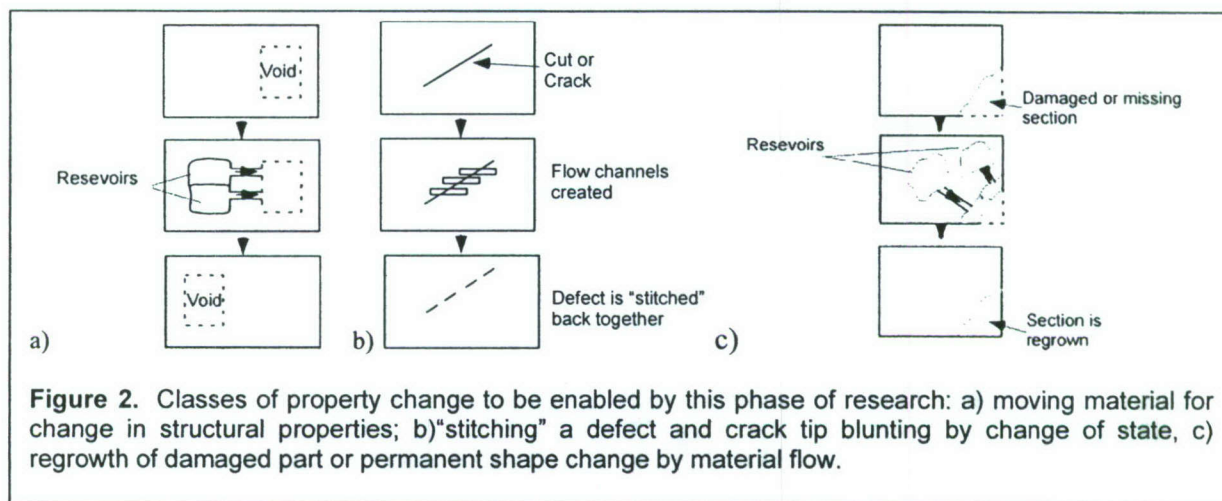
- Reconfigurable flow paths, limited by the resolution of the trigger and pumping mechanisms within the structure;
- Ability to change structural dynamics through solid-to-liquid change, through mass transport, and through “stiffness transport;”
- Ability to transport material along reconfigurable paths for shape change and healing;
- Ability to use the pumping mechanisms as high degree-of-freedom actuators for structural deformation.
- Ability to draw material from one area of a structure to help heal or regrow another area.

#### *Affected Structural Properties*



**Figure 1.** Schematic of reconfigurable circulatory system concept.

The proposed structures will have several classes of property changes. Three key types of changes that will be enabled by this project are shown in Fig. 2, and include change of structural dynamic properties, healing of cracks and defects, and regrowth of damaged or removed areas of



a structure. *Structural Dynamic Properties:* i) a liquid cannot support tensile loads, thus, simply altering the solid-to-liquid proportion will result in the control of directional structural stiffness; ii) by moving material from one region to another, the structural stiffness can be decreased in one region and increased in the other (“stiffness transport”); iii) by moving the mass of a material around in a structure, its modal dynamics can be significantly changed. *Healing:* A defect in a structure (crack or cut) can be “stitched” back together (and possibly completely healed depending on the resolution and orientation of the trigger network) by transforming the surrounding material to liquid and back to solid form. In addition, the tip of a crack may be blunted to prevent further fracture. *Regrowth:* A missing portion of a structure (presumably due to damage) can be reconstituted by drawing from neighboring material. The same concept can be used to permanently change the structure’s shape by flowing structural material to new locations.

### *Research Focus*

This project focused on the primary challenge of this research (reversible solid-to-liquid transition) and on the benefits of such transition and transport in a structure. Each of these areas of research is discussed in more detail below.

## **B.2 Development of Reversible State-Changing Materials**

Two distinct approaches were pursued for developing materials that can exhibit reversible solid-to-liquid transitions, including photo-triggered and electrically-triggered systems. Each of these efforts is described below.

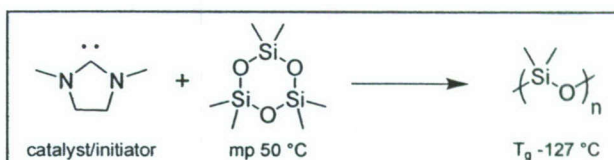
### Research by the Bielawski Group -- Development of Photo-triggered State-Changing Polysiloxanes



Initial efforts focused on establishing a “proof-of-concept” experiment where a solid monomer can be converted into a liquid polymer, ultimately via a photo-induced process. Nucleophilic ring opening-polymerization of

hexamethylcyclotrisiloxane (solid, mp > 50 °C) to afford polydimethylsiloxane [Di Landro et al, 2003] (liquid, viscosities ranging 10 cP for oligomeric materials to over 50,000 cP for high molecular weight

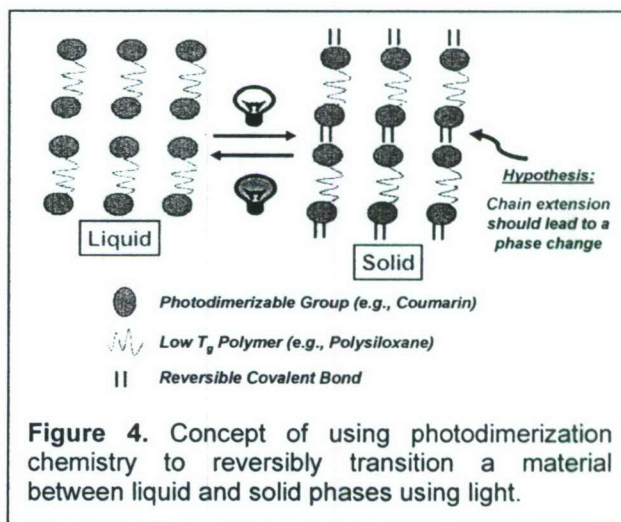
materials) was chosen as the model system, as such polymerizations are known to proceed with good kinetics and control. As shown in Figure 3, initial efforts were directed at using stable N-heterocyclic carbenes (NHCs) [Arduengo et al, 1999], to initiate the polymerization reactions. NHCs are a structurally-diverse class of molecules that have found to be outstanding catalysts for ring-opening polymerizations of a broad range of cyclic monomers [Csihony et al, 2005]. Furthermore, our group has extensive experience in synthesizing and using NHCs in various aspects of macromolecular chemistry [Boydston et al, 2005].



**Figure 3.** Polymerization of hexamethylcyclotrisiloxane to polydimethylsiloxane using a nucleophilic N-heterocyclic carbene (NHC). Melting points (mp) and glass transition temperatures ( $T_g$ ) for representative materials are indicated.

Soon after these efforts were begun, a publication appeared in the literature describing the aforementioned polymerization reaction [Lohmeijer et al, 2006]. In particular, various N-heterocyclic carbenes were combined with different cyclic siloxanes to generate polysiloxanes. In many cases, the viscosities of the materials were shown to *decrease* upon polymerization. While this obviously set a strong precedent for the general concept and aims, it was naturally disappointing not to be the first to report this chemistry.

In parallel with the aforementioned studies, efforts were directed toward developing a system that can reversibly transition between a solid and a liquid using reversible covalent chemistry. The basic concept is illustrated in Figure 4. In essence, liquid monomer is designed to contain pendant functional groups that can react upon exposure to light. The hypothesis is that the chemical reaction should result in dimerization of these groups, and ultimately a large change in molecular weight leading to solidification. If the photodimerization chemistry can be designed such that it is reversible, then the opposite reaction (i.e., solid to liquid) should be possible as well.



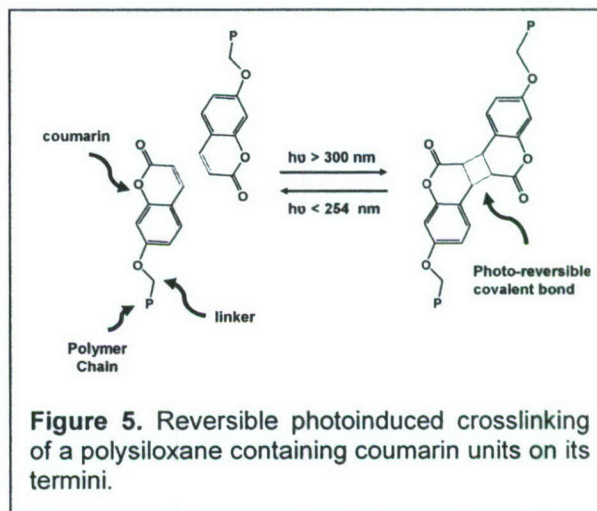
**Figure 4.** Concept of using photodimerization chemistry to reversibly transition a material between liquid and solid phases using light.

It was envisioned that this process may be accomplished by attaching a photodimerizable group to the backbone of polysiloxane that is liquid at ambient temperature. Since reversibility is



essential for a reconfigurable system, the photodimerizable group must possess the ability to undergo a reversible chemical reaction and preferably at a different, but accessible wavelength of radiation. Thus, exposure of these materials to one particular wavelength of light should lead to a crosslinked material; whereas exposure to a different wavelength of light should reverse the crosslinking reaction and reform a liquid material.

Coumarins are well-known to undergo a reversible, photoinduced cyclodimerization upon exposure to radiation and, as a result, have found tremendous utility as laser dyes, agents for alignment of liquid crystals, and photoresists [Trenor et al, 2004]. They have also been found to function as effective reversible photocrosslinkable agents in polyferrocene-based materials [Zhao et al, 2006], greatly increasing the chances that the approach outlined below will be successful. Furthermore, coumarins are readily-available and easy to modify. As illustrated in Figure 5, exposure of a liquid polysiloxane containing pendant coumarin units to light with wavelengths greater than 300 nm should result in a solid crosslinked network. Exposure of the solid network to light with wavelengths shorter than 254 nm should result in a photoinduced [2+2] cycloreversion and re-form its corresponding (liquid-phase) starting material.

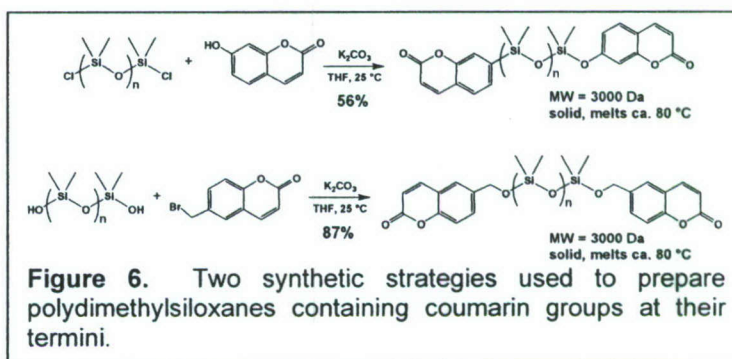


**Figure 5.** Reversible photoinduced crosslinking of a polysiloxane containing coumarin units on its termini.

Two different approaches were employed to synthesize polysiloxanes with pendant coumarin moieties. As shown in Figure 6 (top), commercially-available hydroxycoumarin was condensed with chloro end-functionalized

polydimethylsiloxane under basic conditions. This procedure afforded a coumarin end-functionalized polydimethylsiloxane with a molecular weight of approximately 3000 Da, as

determined by gel permeation chromatography, relative to polystyrene standards. Although this material was a solid at room temperature, it was found to melt at approximately 80 °C. However, the overall yield of this reaction was only 56%. This is largely due to the difficulties encountered in purifying the product as it proved difficult to completely remove unreacted starting material. As a result, a different synthetic methodology to an analogous material was developed. As shown in Figure 6 (bottom), treatment of a commercially available polydimethylsiloxane end-functionalized with hydroxy groups with bromomethylcoumarin resulted in a coumarin end-functionalized polydimethylsiloxane. Notably, this polymer exhibited a similar molecular weight and thermal characteristics ( $T_m = 80\text{ °C}$ ) as the material

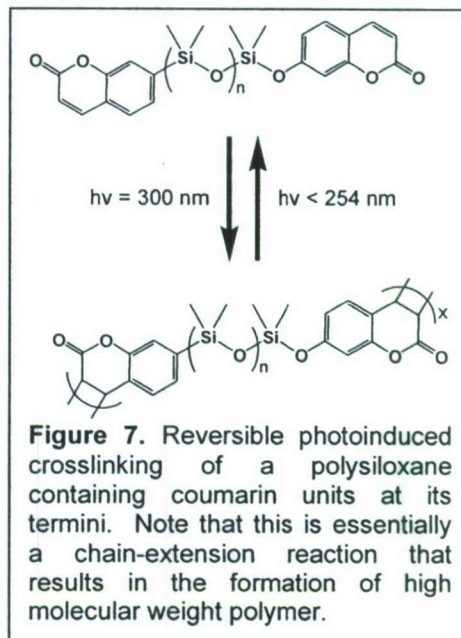


**Figure 6.** Two synthetic strategies used to prepare polydimethylsiloxanes containing coumarin groups at their termini.



described above. At 87%, the overall yield of this reaction was considerable higher than our previous method. However, the disadvantage of this approach is that the bromomethylcoumarin must be prepared. (Although, it can be prepared in very high yields from commercially-available materials.)

With relatively low-melting polydimethylsiloxanes end-functionalized with coumarin groups in hand, efforts shifted toward crosslinking (i.e., polymerizing) these materials using photoinduced dimerization. In general, thin films of these materials were first dissolved in tetrahydrofuran and then exposed to 254 nm radiation for 8 h (see Figure 7). Afterward, the solvent was removed and the resulting material was analyzed by NMR spectroscopy. NMR analysis confirmed that the coumarin groups underwent dimerization as the relative intensity of the olefinic signals were drastically reduced. Furthermore, the bulk material was found to have an increased melting point ( $T_m \sim 110\text{ }^{\circ}\text{C}$ ) and was significantly more viscous in the liquid state than its precursor. Exposing THF solutions of this material to 300 nm radiation for 12 h resulted in re-formation of the initial starting material. Hence, overall, a photo-induced polymerization of polydimethylsiloxanes with coumarin end groups was developed. This process was found to be reversible and resulting in a significant change in the thermal properties of the material. While these results were certainly a big step forward in reaching the ultimate objective, there were two main obstacles: (1) the rates of the forward and reverse photodimerization reactions were very slow ( $\sim$  hours) and (2) a material that was liquid at room temperature was unable to be converted to a solid at room temperature (although, again, a significant change in  $T_m$  was observed upon photo-induced polymerization.)

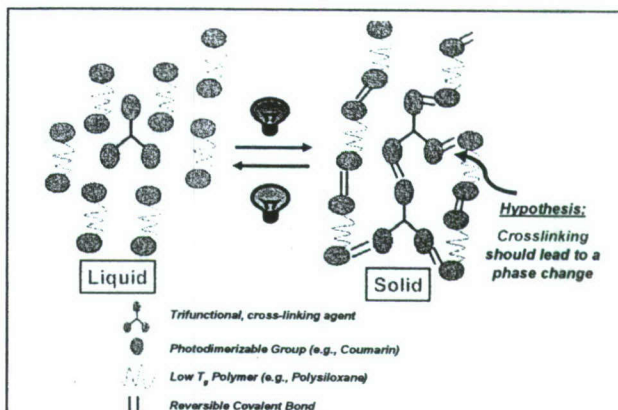


Hence, subsequent efforts shifted toward (1) increasing the kinetics of the photochemistry (i.e., decreasing the time it takes to convert a siloxane-based material from one state to another and (2) decreasing the melting temperature of the siloxane-based material. As summarized in Figure 8, it was reasoned that the addition of a trifunctional crosslinker (i.e., a relatively low molecular weight compound that possessed three coumarin groups, would drastically decrease the time it takes to convert the material from one state to another. (In essence, this compound would be able to link multiple chains together which should lead to a more rapid change in the overall molecular weight of the materials.) In addition, if the trifunctional compound can be designed to be liquid at low temperature, then it could function as a plasticizer and reduce the melting point of the end-functionalized polydimethylsiloxanes as well.

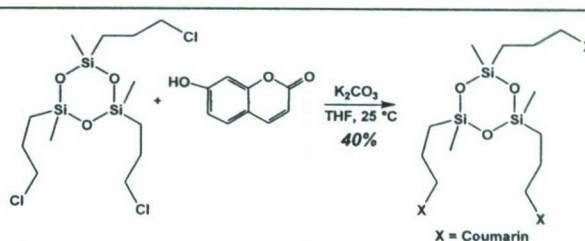


The synthesis of a trifunctional crosslinker is shown in Figure 9. A commercially-available chloropropyl derivative of a cyclic siloxane was treated with hydroxycoumarin under basic conditions to afford the trifunctionalized derivative shown. After synthesis and characterization, this material (10% w/w) was dissolved along with the polydimethylsiloxane end-functionalized with coumarins described above in THF. As summarized in Figure 10, exposing the resulting mixture to 254 nm radiation afforded a gel that precipitated from solution within two hours. Unfortunately, this gel proved to be insoluble in common organic solvents which prevented its full characterization. However, based on the previous results, it is believed that the material is being crosslinked through the photodimerization pathway described above. Attempts were made to try to reverse the crosslinking by exposing the gel to 300 nm radiation for an extended period of time. While small amounts of starting material were found after washing the irradiated gel with solvent, a vast majority remained in its gelatinous form. This suggested that the kinetics of the reverse reaction were slow, likely due to the fact that the bulk material was in the solid state. Regardless, the fact that precipitated material was observed in only two hours indicated to us that the kinetics of the crosslinking reaction was significantly improved.

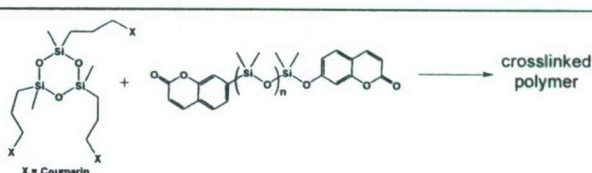
After the last set of results, it became clear that the main problem with each of these approaches is that the materials were not free-flowing liquids at room temperature (which can be expected to exhibit good kinetics, at least for the forward photodimerization reaction). Hence, subsequent efforts focused on synthesizing relatively low molecular weight compounds that would be liquids at room temperature. In particular, efforts were directed at synthesizing simply hydrocarbon based materials. This class of molecules (rather than siloxanes) was chosen to work with because a wide range of functional hydrocarbons exist which would enable quick



**Figure 8.** Concept of using trifunctional crosslinking agents to facilitate the transition of a liquid material to a solid analogue. The trifunctional agent is envisioned to more rapidly connect various polydimethylsiloxane chains containing coumarins at their termini to each other. Hence, the time it takes to convert from a liquid to a solid should be shorter compared to the approaches described above.



**Figure 9.** Synthetic strategy used to prepare a trifunctional crosslinking agent featuring three coumarin groups.



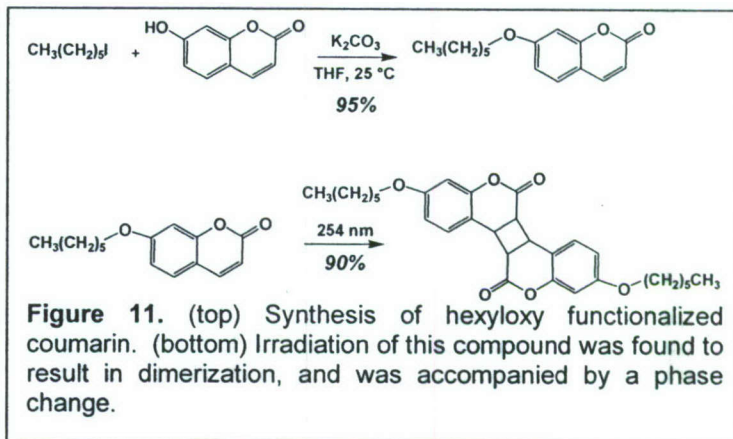
**Figure 10.** Irradiation of a sample containing the trifunctional crosslinking agent and a polydimethylsiloxane with coumarin groups at its termini lead to an insoluble gel which is believed to be a highly crosslinked polymer based on its chemical characteristics (i.e., poor solubility, etc.)



installation groups that could ensure high fluidities, even at low temperatures. While such materials are obviously not polymeric and therefore cannot be expected to display good mechanical properties, a proof-of-concept experiment was sought to show that once a liquid polymer can be obtained, the overall strategy could be successful.

As shown in Figure 11, hydroxycoumarin was condensed with 1-iodohexane under mildly basic conditions to afford a hexyl derivative of coumarin in excellent yield. Notably, this material was found to be a liquid when just a small amount of hexanes solvent was added to it. However, irradiation of this mixture with 254 nm radiation resulted in the formation of a solid within 3 h. (This process was accomplished in

concentrated form, as just described, and also in relatively THF solutions.) The solid material was subsequently treated with 300 nm radiation which caused partial (up to 90%) de-dimerization to obtain the starting material; however, relatively long reaction times (up to 12 h) were required. The reverse reaction was found to be quantitative (100 % yield) when the sample was irradiated in solution, although again, this required relatively long periods of time.



In summary, a range of siloxane and hydrocarbon based materials have been prepared containing coumarin functionalities. In general, irradiation of these materials with light at a certain energy induced a photodimerization reaction which converted them from free-flowing liquids or relatively low melting point solids ( $T_m = 80\text{ }^{\circ}\text{C}$ ) to solids and high melting solids, respectively. In some cases, irradiation of these materials with light at a different energy than the one previously described caused the materials to revert to their original forms. Hence, it is believed that the concept of being able to reversibly convert a liquid to a solid, and back, using light, has been precipitated.

However, these processes are not yet ideal. The forward and reverse chemical reactions are relatively slow and often incomplete. This is believed to be due to poor reaction kinetics, low light transparency through the solid materials, incomplete reaction between complementary coumarin groups, and/or a combination thereof. The most promising results were obtained with the hydrocarbon (i.e., non-siloxane) systems, although these were not polymeric. Hence, future directions should continue along these lines with a primary focus on preparing polymeric analogues. One can envision attaching a variety of long chain, branched hydrocarbons (many of which are commercially-available) to coumarin moieties and repeating the aforementioned experiments and/or the experiments proposed in the initial application. In addition, the use of other photodimerization chemical groups (cinnamates, etc.) may be explored as they may result in faster kinetics which will facilitate transition between solid and liquid forms in shorter periods of time.



## Research by the Beckman Group – Development of State Transition Materials through Electrical Triggers

The overall aim of this part of the experimental program is to design and test a material that can alter its viscosity over a several order of magnitude range (resulting in an effective reversible change of state from solid to liquid) via application of a reversible yet controllable electrical trigger. In this part of the work the use of a redox reaction as the trigger was proposed, where the transfer of electrons inherent to redox chemistry is supplied by an applied voltage, rather than a soluble factor.

Viscosity in bulk polymeric systems generally scales as  $\sim M^3$ , where  $M$  is the molecular weight. In solution, viscosity scales as a polynomial in concentration, where the intrinsic viscosity features in each of the prefactors. Intrinsic viscosity itself is a strong function of molecular weight, typically scaling as  $M^a$ , where  $a$  ranges from 0.6 to 1.0 for good solvents. In summary, the best way to achieve dramatic changes in viscosity, either in a bulk or in a solution situation, is to be able to reversibly alter the molecular weight over a significant range.

Meijer and colleagues in the Netherlands have employed this concept to design materials that can alter their viscosity dramatically using temperature as the trigger. Here, oligomers were synthesized whose end groups could hydrogen-bond with each other. As such, at low temperatures (where the propensity to hydrogen bond is strong), the end groups would associate and the material would adopt properties akin to that of a high molecular weight polymer. As the temperature was raised, the degree to which the end groups would hydrogen bond dropped (as expected) and the material adopted the viscosity one would expect from a low molecular weight oligomer. Hence, the concept for altering viscosity through reversible molecular weight changes is sound, although here it is desirable to employ a trigger other than temperature.

The approach used in this work is to employ reversible redox reactions to change molecular weight in a controllable way and hence induce larger reversible changes in viscosity. While redox chemistry can be performed using soluble reagents, the ultimate goal is to employ applied voltage to trigger the needed chemistry and hence the viscosity change. This was done with some success in this project. There are a number of functional groups whose properties could allow target materials to be fashioned; these include ferrocene, di-sulfides, tetrathiafulvalene, and others. In the following section experiments are described that illustrate the concept that voltage-induced reversible redox chemistry can be used to create materials whose viscosity will change from “fluid” to solid-like upon application of the trigger.

### *Synthesis of the electrically stimulated material*

Polyurethanes have been widely used in machinery, transport, furnishings, textiles, paper-making, packaging, adhesives and sealants, and medicine. The primary reaction for polyurethanes synthesis is the reaction of the isocyanate group with a reactive hydrogen-containing molecule, such as an alcohol, a polyol, an amine or water.

Some organic compounds with two or more mercapto groups have become possible cathode materials with a high energy storage devices, because the two mercapto groups undergo



intermolecular disulfide bonding to become polydisulfides, accompanied by the two-electron oxidation per one disulfide bond and reductive de-polymerization in reverse.

Thiol compounds, such as glutathione, cysteine and homocysteine are a natural reservoir of reductive capacities of the cells. Cysteine, an amino acid, is a critical substrate in biosynthesis of proteins, glutathione, taurine sulfate and the exceptionally metabolically active sulfane sulfur [Iciek and Wlodek, 2001]. Cysteinylglycine is produced as a result of intracellular glutathione hydrolysis by  $\gamma$ -glutamyl transpeptidase, an enzyme which is located on the outer side of plasma membrane. Homocysteine, which is formed from methionine by transmethylation reaction is a precursor of cysteine in the cells, and its elevated plasma level is considered to be an atherosclerosis-promoting factor [McCully, 1996].

The concept of redox status of plasma postulates that there are dynamic interactions between different redox forms of thiol realized through redox reactions, including reactions of thiol-disulfide exchange [Ueland, 1995].

A new generation of poly(urethane-urea) has been developed in this project, which is made up of cysteine based, reversible cure-dissolve materials. Testing of these polymers for their redox reactions was carried out. The pre-polymer was synthesized by lysine diisocyanate, sugar and cysteine. The transitions from the liquid to solid (or solid to liquid) induced either by chemicals or by electrical stimulus were also investigated. A solid gel was obtained from a cysteine-terminated pre-polymer induced either by a thiol-disulfide exchange reaction between cysteine terminated pre-polymer and low-molecular-weight disulfides including cystamine and glutathione disulfide (Scheme I, shown in Figure 12) or by electrical (Scheme II, shown in Figure 13).

Figure 14 shows the effect of the concentration of glutathione disulfide on the polymerization of the cysteine-terminated polymer. In this test, the liquid became a soft solid gel when glutathione disulfide was added into the prepolymer solution, the more glutathione disulfide the more solid gel formed. In the other hand, the addition of the reduced type glutathione induced the solid dissolution (Figure 15).

Similar results were obtained by electrical stimulus. When two electrodes were immersed in the same pre-polymer solution and voltage was applied, the solid appeared on and between two electrodes immersed in the solution (Figure 16). The material remained in the solid state after the removal of the electric field; reversing the polarity of the originally applied field partially returned the material to its liquid state. In its present form this property changing material is in fact responding more to electrochemistry than to electric field.

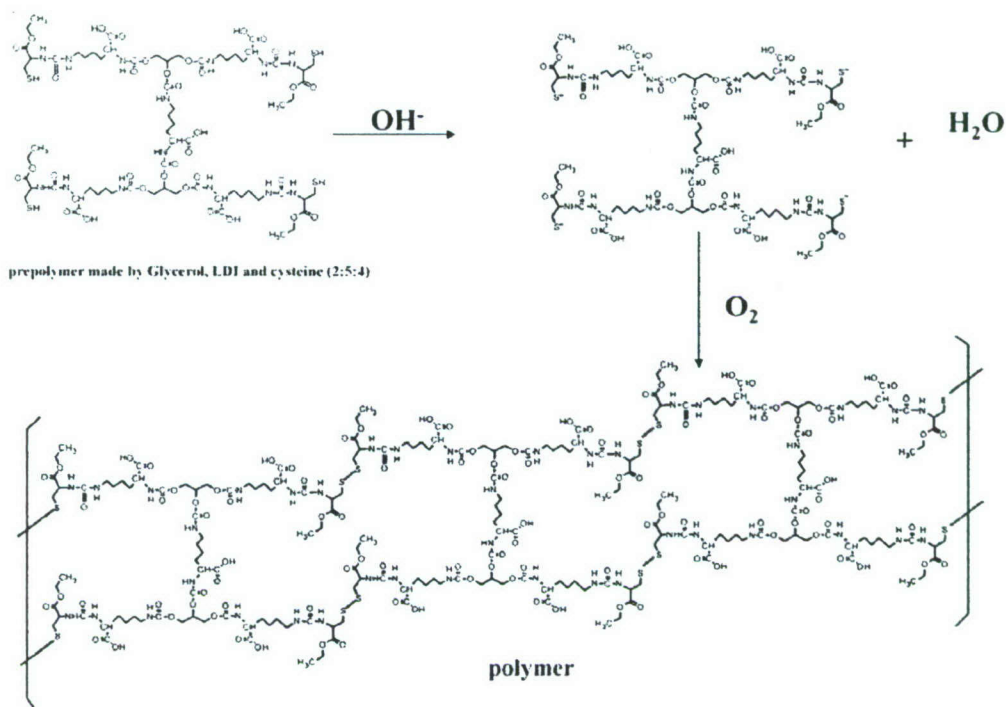
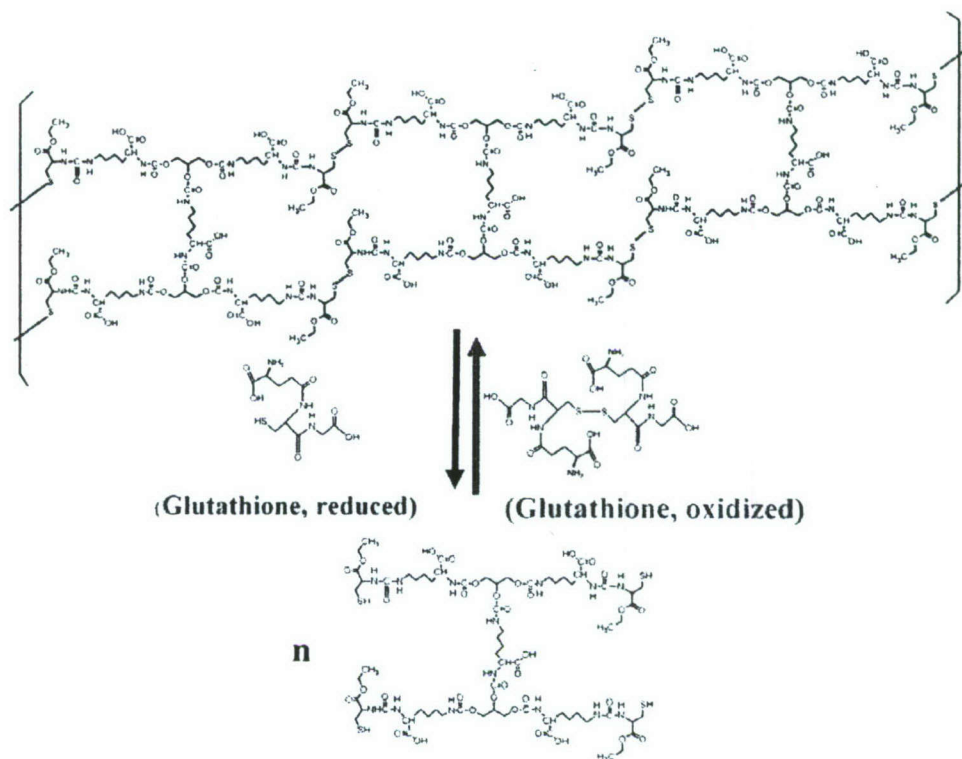
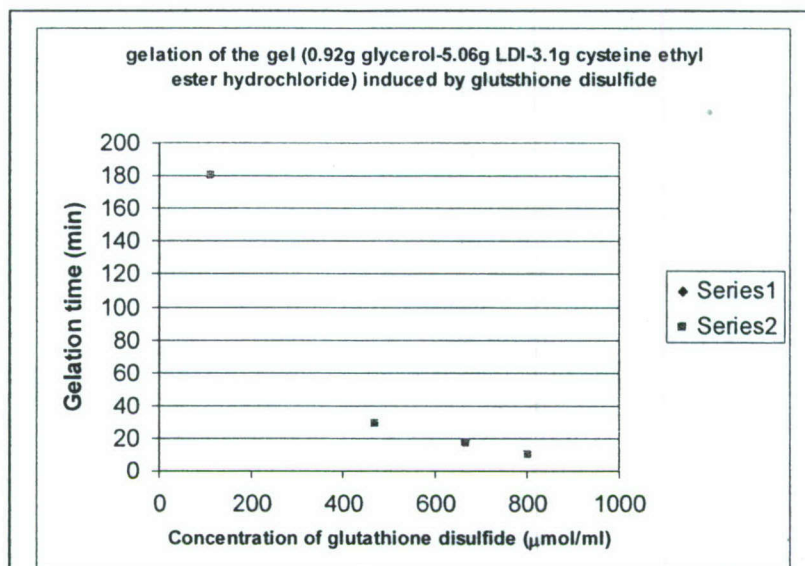


Figure 12. Scheme I: Cross-linking reaction for cysteine terminated LDI-glycerol polymer.

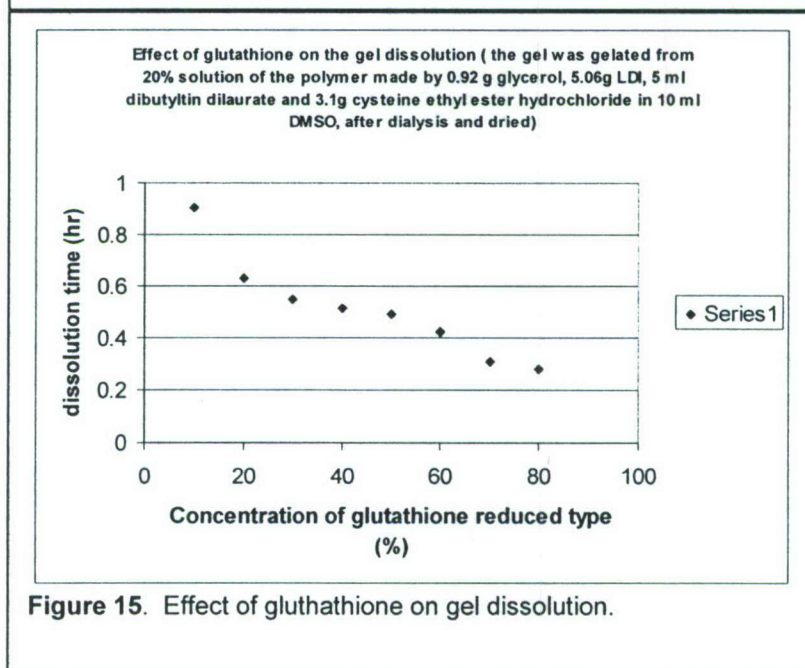




**Figure 13.** Scheme II: Dissolution-gelation of Cysteine terminated LDI-glycerol polymer gel.



**Figure 14.** Polymerization time of cysteine-terminated polymer induced by glutathione disulfide.

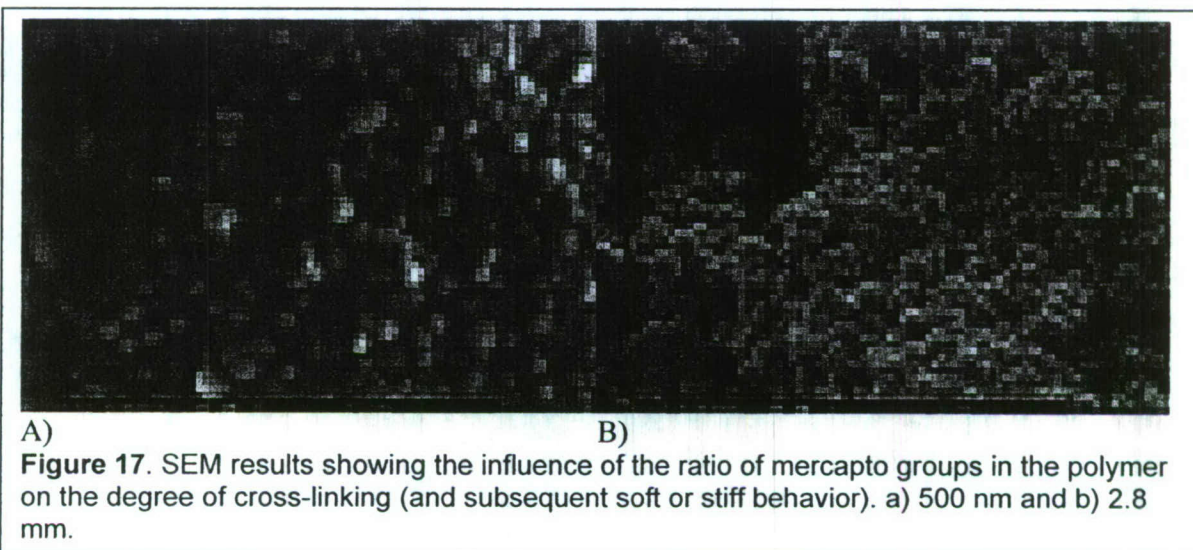
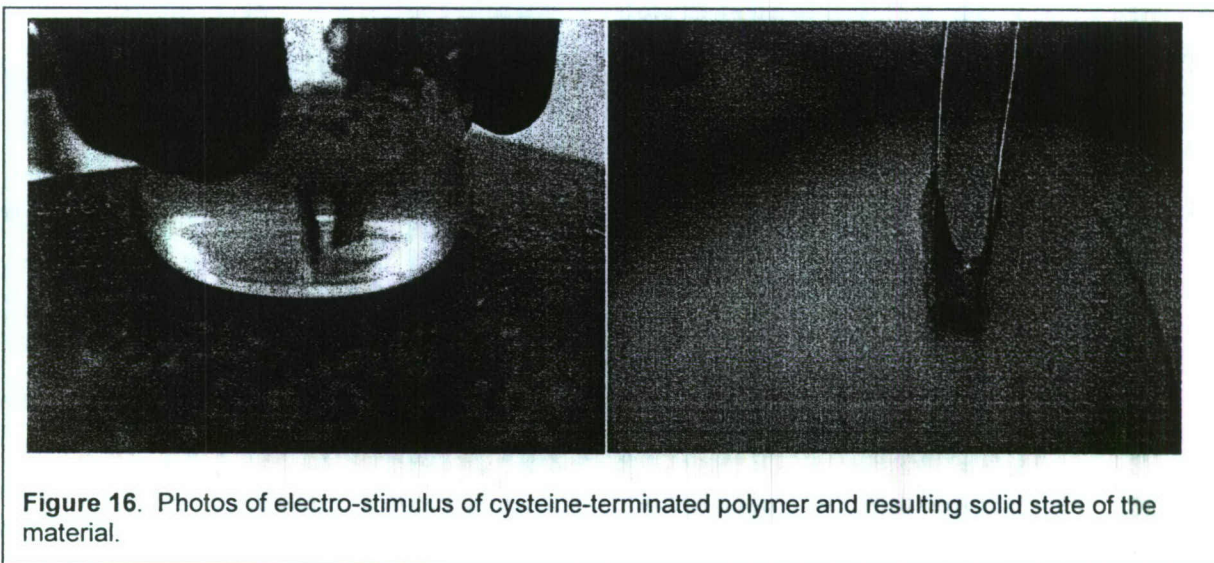


**Figure 15.** Effect of glutathione on gel dissolution.

SEM results showed that different ratios of the mercapto groups in the polymer influenced the cross-linking degree of the polymer (soft or stiff). The more mercapto groups contained in the polymer, the higher degree of cross-linking and the smaller pore/particle size of the polymer was obtained. The average diameters of the particles were about 500 nm (Figure 17A) and 2.8  $\mu\text{m}$  (Figure 17B), respectively. Two polymer gels were made by Tris, LDI and cysteine ethyl ester hydrochloride. The sample A was obtained by a ratio of Tris:LDI:cysteine = 2:7:6. and sample B was obtained by a ratio of Tris:LDI:cysteine = 1:4:4. The SEM samples were prepared by adding 0.3 ml of 1 N NaOH into 0.6g above solutions which dialyzed against water, and the obtained gel



was dried at room temperature and sputter coated with gold/palladium. The samples were examined under a Joel Scanning microscope with an accelerating voltage of 5 kv.



The preliminary data in this study indicates that the cysteine-terminated pre-polymer can be cured by redox reaction either induced by chemical oxidants or by electrical stimulus. Furthermore, the polymerization induced by electrical stimulus is faster, easier and cleaner (without by-products).

For future work it is suggested to design various mercapto-based reversible cure-dissolve polymers. It is hypothesized that the application of electrical stimulus will encourage the polymer gel/film/foam formation and the structures of the polymer gel/film/foam induced by electrical stimulus should be more homogeneous and controllable than those induced by chemicals. In addition, it is possible to modify the existing material concept such that it will



transition between relatively stiff and soft solid states (as opposed to liquid to soft-solid transition).

### **B.3 Analysis of Structural Property Changes by way of Reconfigurable Circulatory Systems**

Just as biological systems utilize circulatory systems for a variety of purposes, such as respiration, transport of fuel and wastes, healing, and heat transfer, there are many potential uses for such systems in man-made structures as well. One could design structures with built-in, predetermined flow paths for transporting materials for the above applications. For structures that undergo significant shape changes, however, it may be more beneficial for the circulatory system to also be reconfigurable rather than being fixed.

The above sections discussed research directed at developing materials that enable structural change through a transport process, this section focuses on the structural properties that can be affected by transporting unloaded mass (mass transport) as well as loaded mass (termed “stiffness transport”).

The section is structured to walk the reader through increasingly complex scenarios of transport capabilities within a structure, discussing the types of structural properties that are enabled with each one. The scenarios include being able to:

- add or subtract non-load-bearing mass in a structure
- move non-load-bearing mass in a structure
- add or subtract load-bearing mass (stiffness) in a structure
- move load-bearing mass (stiffness) in a structure

The fact that mass and stiffness distribution in a structure affects its dynamic properties is well understood (there are many vibration texts on the subject (Rao, 1990; Thompson and Dahleh, 1998; Inman, 1998)). The concept of properly distributing mass and stiffness has been used for vibration control methods in the past through active and passive eigenstructure assignment (for example, (Fahmy and O'Reilly, 1982; Hodges, 1982; Yigit and Choura, 1995, Shelly and Clark, 1996)). It is argued here that the fourth scenario above, stiffness transport, enables all of the properties afforded by the previous three scenarios, along with additional, unconventional capabilities in structures. This section concludes with a numerical example of stiffness transport to illustrate several potential changes in structural properties.

#### **What Structural Change can be Accomplished if Mass Is Added or Removed?**

The first question is somewhat hypothetical, in that it is difficult to autonomously add or remove mass in a structure because the mass must go to somewhere or come from somewhere that is not a moving part of the structure. Nonetheless, if one were to disengage mass from a structure or to add mass to a structure, then the following structural characteristics can be changed:

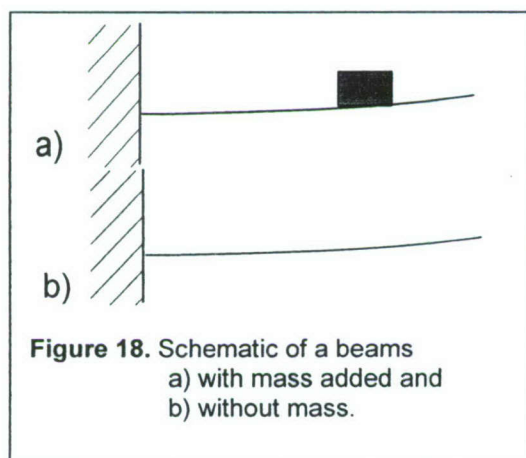
- Natural Frequencies
- Mode Shapes
- Shape (weak effect)



Assume a cantilever beam shown in Figure 18a in which a slug of mass is attached at some point along the length. The natural frequency for any mode of the beam can be written in general terms as

$$\omega = \sqrt{\frac{k_{eff}}{(\alpha m_{beam} + \beta m_{slug})}} \quad (1)$$

where  $k_{eff}$  is the effective stiffness for that mode,  $m_{beam}$  and  $m_{slug}$  are the beam effective mass and slug mass, respectively, and  $\alpha$  and  $\beta$  are factors that depend on the mode number and the location of the mass (for example, Rao, 1990; Thompson and Dahleh, 1998; Inman, 1998).



**Figure 18.** Schematic of a beams  
a) with mass added and  
b) without mass.

The mode shapes of the structure can also be changed. In general the mass, if large enough in relation to the rest of the structure, will tend to create a node point in the structure. As the mass is removed this point will see more freedom to move.

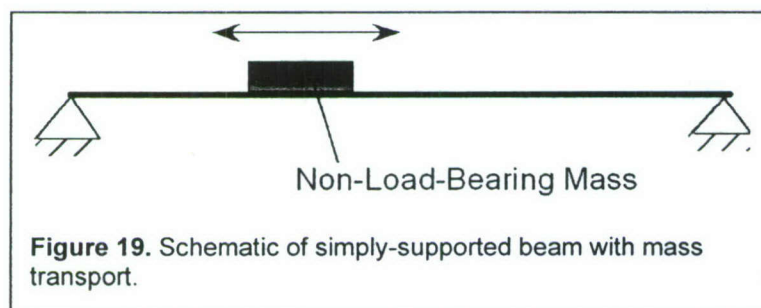
Finally, the shape of the structure is affected by adding or removing mass, although this is a weak effect. Obviously the mass takes up space, so adding or removing the mass has an effect on the overall shape of the structure, however the fundamental underlying structural shape (which defines its ability to support loads in space) is not significantly

changed.

### What Structural Change can be Accomplished if Mass is Moved Within a Structure (Mass Transport)?

A)

This question assumes that the mass can be moved in the structure by some mechanism, and the mass that moves does not contribute to the stiffness of the system, but rather only to its inertial properties. Since the dynamic behavior of a structure depends on both its distributed mass and stiffness properties, one can exert significant control over a structure's behavior by moving mass within the structure.



**Figure 19.** Schematic of simply-supported beam with mass transport.

Figure 19 shows an example in which a simply-supported beam carries a slug of material that can be moved to any position along the length of the beam. The structural characteristics that can be affected by moving the mass can once again be listed as:

- Natural Frequencies
- Mode Shapes

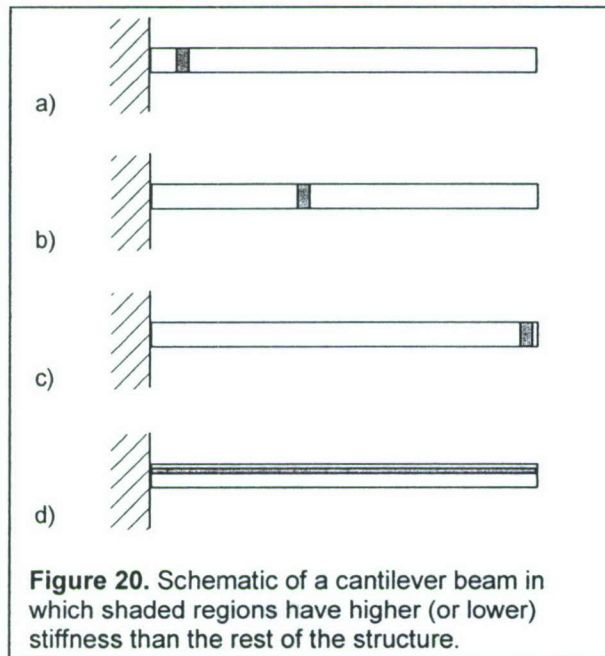
- Shape (weak effect)

This list assumes, for this immediate discussion, that the slug cannot contribute to the stiffness of the beam, but only to its inertial properties. The beam clearly has different mode shapes and natural frequencies as the mass is moved from one of the ends to the center. Equation 1 can be used to capture this effect (for beam frequencies) where in this case the  $\beta$  term is now adjusted instead of simply adding or removing  $m_{slug}$ . Note that if the mass were to be moved completely to one of the supports, it has been effectively removed from the dynamics of the structure, which is the special case of the previous question. Also, the shape is only weakly affected by moving mass in the context shown here since the underlying structural integrity is not changed by moving non-load-bearing mass.

### What Structural Change can be Accomplished if Stiffness is Added or Removed?

Now consider the case in which stiffness elements can be added or removed within a structure. This scenario is depicted by Fig. 20, which shows a cantilever beam that has certain regions made up of material that is stiffer (or less stiff) than the rest of the material within the beam. In this scenario, the following structural characteristics can be changed:

- Natural Frequencies
- Mode Shapes
- Strength / Deflected Shape



The authority over natural frequencies and mode shapes is not unlike that achieved by adding or removing mass. The effective stiffness of Eq. 1 is changed by adding or removing stiffness within a structure. For the cantilever beam shown in Fig. 20, decreasing the stiffness near the base (case a) has a much more significant effect on  $k_{eff}$  than decreasing the stiffness near the free end (case c). Likewise, the mode shapes of the structure vary depending on what region sees an increased or decreased stiffness. In an extreme case, if one were to allow the stiffness to go to zero in the shaded region in Fig. 20a, then the beam no longer exhibits cantilevered mode shapes, but it is effectively a free-free structure of slightly shorter length (it is cut off from the clamped support).

While the authority over the structure's dynamic properties (frequencies and mode shapes) is similar for adding or subtracting stiffness as it is for modifying mass, the ability to affect the nominal shape has been lost in this scenario. For example, in each case of Figure 20 the nominal shape of the structure is unchanged. Simply increasing or decreasing stiffness in local regions does not affect the nominal shape as adding or removing mass does. However, as discussed



above, this is only a weak effect in that case, and would only be considered as a method of shape change when minor changes are needed. Finally, adding or removing stiffness enables a new characteristic that can be change in a structure: strength.

The overall strength of a structure is dependent upon the distribution of material elastic modulus within it, which includes both the geometric distribution and the modulus values at given points. In this case, control over the modulus value at specific locations within the structure is assumed. By changing these values, one can affect the nominal strength of the structure. While the strength itself is not related to the nominal (unloaded) shape of the structure, it clearly affects the loaded shape. For that reason, one can affect the operating (loaded) shape of a structure by adding or removing local stiffness within it.

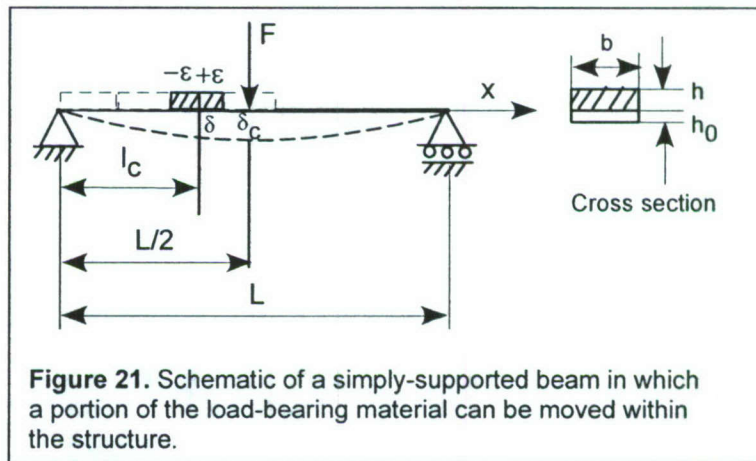
For example, if one were to apply a tip load to the beam in Fig. 20, under the conditions in which the whole beam is of nominal stiffness, a given deflection would be generated. By lowering the stiffness in any of the shaded regions depicted in cases a-d), however, much greater deflections would be observed for the same applied tip load (with cases a and d possibly seeing the highest deflections).

#### What Structural Change can be Accomplished if Stiffness is Moved Within a Structure (Stiffness Transport)?

Now consider the case in which an element or region of a given stiffness can be moved within a structure, as depicted in Fig. 21. This figure is similar to that shown in Fig. 19, but rather than the slug simply being a moveable mass, now it is an element of stiffness (a load-bearing mass). This process is defined as “stiffness transport,” which is the geometric displacement of load-bearing capability within a structure. For the example shown, it could be a component that is securely fastened to the beam, thus changing the beam’s effective rigidity over the length of the component. The placement of the component, then, affects not only the beam’s static deflection to a load, but also the dynamic behavior. In this scenario, the following structural characteristics can be changed:

- Natural Frequencies
- Mode Shapes
- Strength / Deflected Shape
- Shape (Morphing)

As in all the other scenarios above, the natural frequencies and mode shapes of the system can be changed. Obviously by moving the element not only is the mass being moved in the structure, but its stiffness is also being rearranged, which both directly affect the eigenstructure.



In addition, the strength and deflected shape of the structure are affected by moving stiffness within the structure. The beam stiffness can be found, along with the appropriate matching and boundary conditions, for the deflection at the midspan of the beam in Fig. 21 for a given applied static load. For a small element (height  $h/h_0 = 3$  and length of  $2\varepsilon/L=1/15$ ) the stiffness can be increased by 50% by moving the material from one end of the beam to the center.

By moving load-bearing material, one can not only affect the strength of the structure, but the nominal shape as well. In this scenario mass and stiffness are inherently coupled, so by “transporting stiffness” one is also transporting mass, and realizing the associated change in shape that comes with it (i.e. the beam changes shape as the load-bearing slug in Fig. 21 moves across the beam just as it does for the moving slug in Fig. 19). In addition, this scenario enables more drastic change in nominal shape of the structure since the material that is move has the ability to carry load after transport, so not only can the basic unloaded shape of the structure be changed or morphed, but the load-bearing geometry can be changed as well.

In addition to the basic set of characteristics that can be changed, stiffness transport also enables two new features:

- Healing
- Growth

Neither of these last two features would be considered to be common (or even possible) features of most nonliving structures. If one were able to move load-bearing material, however, then a damaged portion of a structure could be repaired through the filling of a hole or the patching of a crack by transporting “healthy” material from one region (presumably one that is not in a critical load path) to another region that is damaged.

An extension of this concept is a case in which load bearing material is transported to occupy a previously unfilled region in space. In this way the structure would have permanently changed its shape by growing or morphing into a new shape. It is assumed that the new shape is required to carry loads (a primary function of the structure) so load bearing material is required in the transport process.

As shown by this list, the transport of load bearing material, or “stiffness transport” can enable not only the basic static and dynamic structural property changes afforded by mass transport, but it also enables a host of other capabilities that are generally not possible with conventional structures.

#### Numerical Example

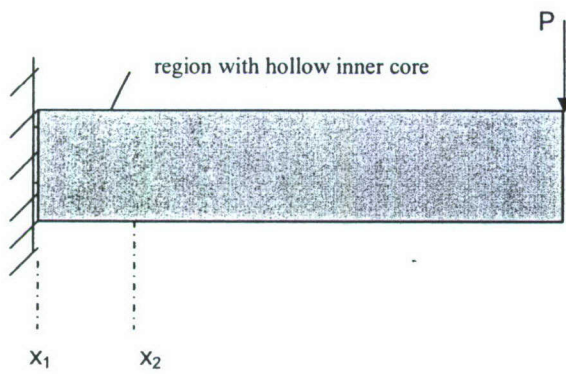
To illustrate the concept of stiffness transport, a numerical simulation of moving material in a cantilever beam will be carried out. Figure 22 shows a cantilever beam, with applied load  $P$ , that has a region of missing material that causes the beam to be weaker than it would be if the region were filled.

Assume the beam properties to be:

length, width and height = 10, 1, and 1 m, respectively



density = 2.7 g/cm<sup>3</sup>  
 Young's modulus = 109 Pa  
 $x_1$  and  $x_2$  = 0 and 1 m, respectively  
 $x_3$  and  $x_4$  = 7 and 8 m, respectively  
 $P$  = 10 kN



**Figure 22.** Schematic of a cantilever beam with a void at the base.

In order to stiffen the beam, the material is transported from near the free end of the beam (a less critical area for supporting the load or contributing to the dynamic stiffness) and placed in the void. This is also stiffness transport, since it is assumed that this material has load bearing properties before and after transport.

The first step in the process is depicted in Fig. 23 in which a reservoir region and a flow path is generated in the structure. These regions now have modulus of zero (this is also an example of the third scenario discussed above, in which stiffness is removed from the structure), so the new beam deflection and equivalent stiffness are found to be:

$$\delta = 9.3 \text{ mm}$$

$$k_{eff} = 1.08 \times 10^6 \text{ N/m}$$

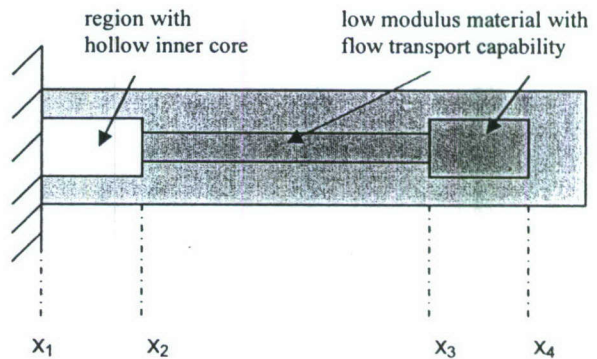
which are only slightly different (higher deflection because of lower stiffness) from the original values since the regions in which stiffness is removed are not critical for supporting the load. The approximate fundamental natural frequency for the beam is now found to be 11.08 Hz (also only slightly changed from the original value).

A number of techniques can be used to calculate the static deflection and dynamic properties of the beam. For this example the area-moment method is used (Popov, 1999). For the nominal structure shown in Fig. 22, the deflection and equivalent stiffness are found to be:

$$\delta = 9.0 \text{ mm}$$

$$k_{eff} = 1.11 \times 10^6 \text{ N/m}$$

The approximate fundamental natural frequency for this beam is found to be 11.25 Hz.



**Figure 23.** Schematic of a cantilever beam prepared for stiffness transport.

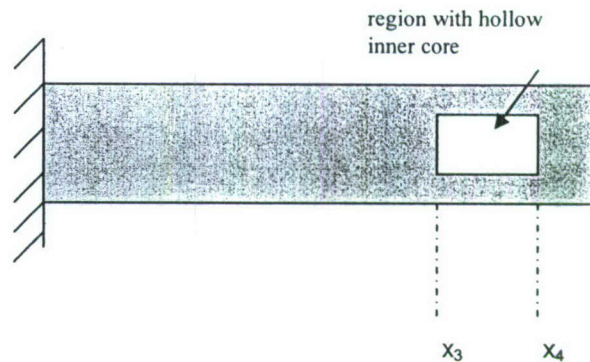
Finally, once the material has been transported to fill the original void, the beam appears as shown in Fig. 24. In this case the new beam properties are:

$$\delta = 4.3 \text{ mm}$$

$$k_{eff} = 2.30 \times 10^6 \text{ N/m}$$

which corresponds to an approximate natural frequency of 16.2 Hz.

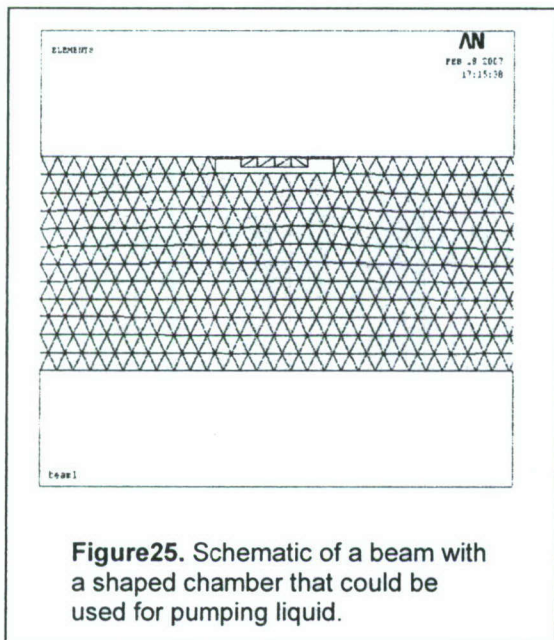
Each of these numbers is substantially different from the original value, but only the natural frequency could have been changed by moving mass alone. The example illustrates that significant changes in both static (strength, deflected shape) and dynamic (natural frequency) properties can be achieved through “stiffness transport.” In addition, the filling of the void in the beam is representative of healing damage that is present in the beam.



**Figure 24.** Schematic of a cantilever beam with a void now moved near the free end of beam.

#### Passive Transport Within a Structure

The concept of reconfigurable circulatory systems within structures (as presented here) depends on the ability to change the state of materials, but it also requires a reliable pumping mechanism for transporting mass (or stiffness, as discussed above). The possibility of using the structure's own motion and stress distribution to pump materials was investigated.



**Figure 25.** Schematic of a beam with a shaped chamber that could be used for pumping liquid.

Figure 25 shows a possible design of a pumping chamber within a beam (shown as a small void at the top of the beam). This design was modeled and analyzed in two dimensions using the finite element method. As the beam deforms (due to vibrations or external loading) the internal chamber will deform. These geometrical changes can be utilized to pump fluid. This design may allow material to be transferred without any externally powered device (electric pump, etc.).

Initial results are shown in Figures 26 and 27. These figures show the deformation of the void as the beam is deformed (note that the beam deformation is exaggerated by the finite element code for clarity). An area change of 15% is produced within the pumping void. Further analysis can provide an optimized geometry that produces a larger volume change. In addition,



different geometries may be appropriate for other boundary conditions (cantilever, clamped-simply supported, etc.).

**Figure 26.** Finite element results showing squeezing of the chamber as the beam deflects.

**Figure 27.** Finite element results showing expansion of the chamber as the beam deflects.

Finally, Figures 28-30 show a network of cavities that are connected in such a way that fluid could conceivably be pumped from one location to another within the beam. The channels and chambers are strategically placed and connected so that the chambers act as mechanical pumps and valves. Initially the channels, chambers, and reservoir are full of fluid. As the beam vibrates (or is loaded cyclically in opposite directions), fluid is moved from one chamber to the next as the respective chambers expand and contract, and ultimately from the reservoir to the void.

**Figure 28.** Step 0: Initially chambers, channels, and reservoir are created (the proposed approach is to create liquid volumes by state change of the structural material). Chambers would be created in such a way to allow desired directional flow of material.

**Figure 29.** Step 1: As the beam is deflected upward, the chambers squeeze and/or open to cause fluid to move toward the void.



**Figure 30.** Step 2: Beam moves in opposite direction and fluid is drawn from reservoir to refill channels. The process repeats on the next deformation cycle.

### **C. Summary**

This project investigated the concept of reconfigurable circulatory systems in which structural material is transformed from solid to liquid state, and then moved within a structure. The uses of this concept include, in the most basic sense, structural shape and structural dynamic property change. More sophisticated applications could include repair of structural damage and regrowth of missing parts.

Two basic elements need to be developed to realize the concept, namely materials that can exhibit the reversible state change, and pumping mechanisms. Both of these were explored in this project, although most of the emphasis was placed on the development of state-changing materials. Photo- and electrically-activated materials were explored, with success being achieved in each case. More research is needed to make the techniques practical by increasing the moduli of the materials and decreasing the speed of response.

Analysis was done to illustrate potential structural changes that could be achieved by this concept, and preliminary approaches were studied for transporting the materials.

In summary, materials that exhibit reversible solid-to-liquid state change would have tremendous value for structural control, shape change or morphing, structural dynamics and static strength tailoring, healing, and potentially growth of parts. In addition, the results of the new materials development in this seed project were promising, and suggest that with more research into the

state-changing materials, near-term low modulus applications could be realized. In the long term higher-strength structures could exhibit these properties.

## **D. References**

- Arduengo, III, A. J. *Acc. Chem. Res.* **1999**, 32, 913.
- Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, 127, 12496.
- Csihony, S.; Culkin, D. A.; Sentman, A. C.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, 127, 9070.
- Di Landro, L.; Levi, M.; Nichetti, D.; Consolo, A. *Eur. Poly. J.* **2003**, 39, 1831.
- Fahmy, M.M., O'Reilly, J., "On eigenstructure assignment in linear multivariable systems," IEE Transactions on Automatic Control, vol. **AC-27**(3), 1982.
- Hodges, C.H., "Confinement of vibration by structural irregularity," *Journal of Sound and Vibration*, **82**(3), 411-424, 1982.
- Iciek M, Wlodek L. Biosynthesis and biological properties of compounds containing highly reactive sulfoxide sulfur. *Pol J Pharmacol* **2001**;53:215-225.
- Inman, D. J., *Engineering Vibration*, Prentice-Hall, Upper Saddle River, New Jersey, 1998.
- Lohmeijer, B. G. G.; Dubois, G.; Leibfarth, F.; Pratt, R. C.; Nederberg, F.; Nelson, A.; Waymouth, R. M.; Wade, C.; Hedrick, J. K. *Org. Lett.* **2006**, 8, 4683.
- McCully KS. Homocysteine and vascular disease. *Nat Med* **1996**;2:386-389.
- Popov, E. P., *Engineering Mechanics of Solids*, Second Edition, Prentice Hall, 1999, p. 635-650
- Rao, S. S, *Mechanical Vibrations*, Addison-Wesley, Reading, Massachusetts, 1990.
- Shelley, F.J. and W.W. Clark, "Eigenvector Scaling for Mode Localization in Vibrating Systems," *AIAA Journal of Guidance, Control, and Dynamics*, Vol. 19, No. 6, pp. 1342-1348, 1996.
- Thomson, W. T. and M. D. Dahleh, *Theory of Vibration with Applications*, Prentice-Hall, Upper Saddle River, New Jersey, 1998.
- Trenor, S. R.; Shultz, A. R.; Love, B. J.; Long, T. E. *Chem. Rev.* **2004**, 104, 3059.
- Ueland PM. Homocysteine species as components of plasma redox thiol status. *Clin Chem* **1995**;41:340-342.



Yigit, A., and Choura, S., "Vibration confinement in flexible structures via alternation of mode shapes by using feedback," *Journal of Sound and Vibration*, **179**(4), 552-568, 1995.

Zhao, D.; Ren, B.; Liu, S.; Liu, X.; Tong, Z. *Chem. Commun.* **2006**, 779.